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Surface Modification of Silver Thin Films Using Low Power Chlorine Plasmas

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Modification of silver thin films to create Ag/AgCl thin film electrodes, using a plasma process, was investigated and the efficiency of the plasma technique was assessed. X-ray photoelectron spectroscopy measurements revealed the presence of AgCl within the thin film after plasma treatment. The observed binding energy peak shifts corroborated with values found in literature. Auger spectroscopy depth analysis showed that, under low input power conditions, the plasma process is controlled by the chlorine flow and the chamber pressure. The quantity of Cl integrated into the silver matrix increased with increasing chamber pressure.
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Silver chloride is an important material as an electrochemical electrode sensor, typically fabricated by screen printing of silver loaded inks followed by chemical chloriding¹ or electrochemical chloriding.² In order to develop microsensor arrays based on Ag/AgCl, a thin film approach is required, but electrochemical chloriding of such films can lead to their destruction. There have been very limited attempts to create Ag/AgCl electrodes via thin film compatible techniques and no satisfactory outcome has been established so far. Indeed, chemical chloriding of thin films, which offers very restricted process control, was shown to be surface limited, while deposition under vacuum of AgCl barely achieved satisfactory electrode characteristics.³ Chlorine-based plasmas⁴ have found widespread use in thin film and semiconductor materials etching.⁵ More recently there have been attempts to understand and control the plasma chemistry making sensitive modification of surfaces a possibility.^{6,7} In this paper, we investigate the use of chlorine plasma processing as an alternative to chemical/electrochemical techniques for partial surface conversion of Ag to AgCl. Plasma exposed Ag was examined by X-ray photoelectron spectroscopy (XPS) and Auger analysis to evaluate species formation at and below the surface.

Experimental

Silver thin films underwent plasma immersion in a PlasmaTech reactive ion etch (RIE) 80 capacitively coupled radio frequency (rf) plasma system, with a 17 cm diam driven electrode. Plasma conditions were 10 to 60 W nominal input power, for 5 to 240 s, at chlorine gas flow 3 to 30 cm³/s. The samples were placed on the driven electrode and the dc bias was 10 V. XPS investigations were carried out on a Kratos XSAM 800 apparatus. The X-ray source was run with Mg K α X-rays at 240 W (13.8 kV, 18 mA). Auger analysis was performed with a Nanosonde Auger Cameca (Nanoscan 100) which includes an argon ion canon for etching and depth analysis purposes.

The samples were etched for various times, and the depth in each case was calculated using an estimated etch rate of 0.7 nm/s, determined from a complete etch on a sacrificial sample of known thickness. Step heights of Ag and modified Ag thin films were measured using a mechanical step profiler (Talystep). The typical sample thickness was around 100 nm, before being processed.

Results and Discussion

Samples were first exposed to a chlorine gas environment similar to the plasma run conditions, but no observable chloriding occurred during a typical run duration (30 s). Although measurements performed after plasma treatment indicated little or no etching of the thin film, interestingly, some increase in thickness was indicated. At the highest values of power and flux, thickness increases of up to

170% were observed. XPS measurements showed that, within the energy range 0–1100 eV, the only detected surface species were Ag and Cl.

Figure 1 shows such a survey scan, wherein the dominant peaks were Ag 3p, Ag 3d, and Cl 2p, along with Auger peaks Ag MNN and Cl LMM. The binding energy (BE) peak shifts were measured and compared to values in the literature, as summarized in Table I. The BE values of chlorine are obtained from NaCl and KCl compounds,⁸ which have an electronic structure close to that of AgCl^{9,10} and hence, comparable BE values.¹¹ Notwithstanding the small BE shifts values (± 0.4 eV) and the difficulties with XPS resolution, it is clear that modified thin films show a similar structure for both Cl and Ag, as found with a standard AgCl powder.¹² However, it is possible to distinguish both compounds by their respective Ag MNN Auger lines. Measurements of Ag Auger peak from a pure Ag thin film gave 895.5 eV. The measured AgCl data showed a BE peak shift at 897.8 eV, corresponding to an experimental positive shift of +2.3 eV.

In order to obtain information on how the composition changes within the thin film, Auger profiling was carried out. Each scan was taken after etching the surface with an Ar⁺ ion beam. With the range of energies (0 to 600 eV), the only detected surface species were Ag and Cl, which both presented narrow peaks, apart from one sample that exhibited carbon impurities. The Cl relative intensity decreases with depth up to a value beyond which no Cl was detected. This analysis was repeated for a range of process conditions. Figures 2a and b represent the variation in Cl penetration depth, calculated from the etch rate, with power and Cl₂ flow, while Fig. 2c shows that the Cl penetration increased approximately linearly with gas flow up to 230 nm at 30 cm³/s. The change in pressure over this flux range

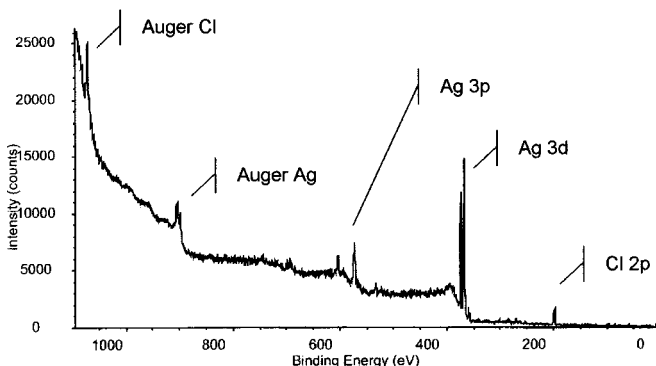


Figure 1. XPS spectra of a plasma modified Ag TF featuring Ag 3d_{5/2}, Ag 3d_{3/2}, Cl 2p_{3/2}, and Cl 2p_{1/2} binding energy peaks, and the Ag MNN and Cl LMM Auger peaks.

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Table I. XPS lines of silver and chlorine in various environments, and their peak shifts.

Molecular orbital	Pure Ag ⁸	Unmodified Ag TF	Alkali chlorine ⁸	AgCl powder ¹²	Plasma modified Ag TF
Ag 3d _{3/2}	374.3	374.61	-	-	374.1
Ag 3d _{5/2}	368.27	368.56	-	368.1	368.2
Ag MNN	895.9	895.5	-	898.2	897.8
Cl 2p _{1/2}	-	-	200.1	200.0	199.9
Cl 2p _{3/2}	-	-	198.5	198.4	198.4

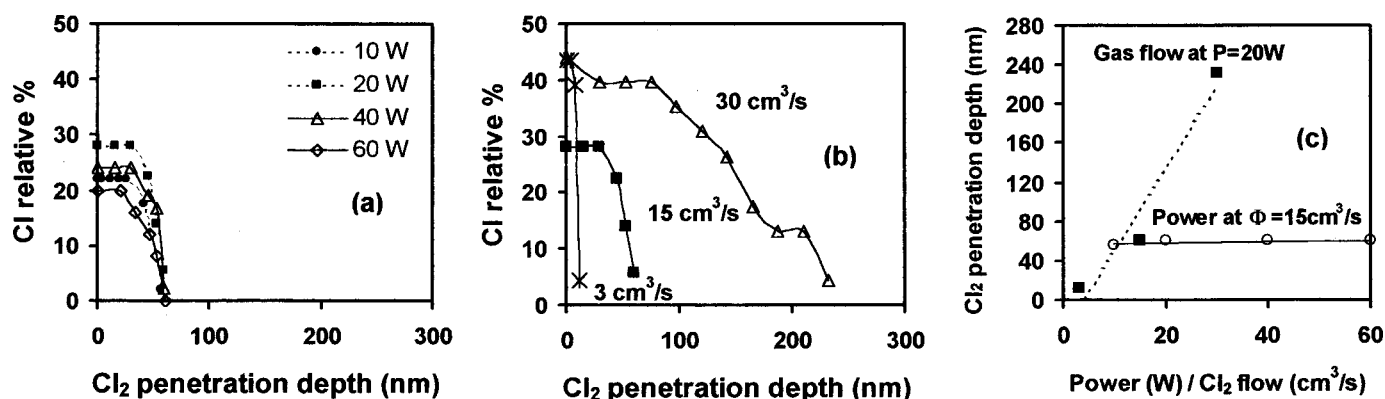


Figure 2. Calculated chlorine penetration depth variation with (a) power, (b) chlorine flux, and (c) corresponding chlorine depth penetration against plasma parameters.

was not significant. The chlorine penetration depth was found to be between 50 and 60 nm and independent of power.

The relative percentage of atomic Cl and Ag is determined by integrating the respective peak areas from the corresponding first derivative Auger spectra ($\epsilon dN[\epsilon]/\epsilon$). In Fig. 3, the variation in surface Ag and Cl is shown as a function of plasma exposure time for 20 W, 15 cm³/s. The Cl fraction increases rapidly to about 30% within 10 s, saturating at around 40% over the following 120 s. At 60 s of processing, a chlorine percentage larger than the corresponding Ag one was found. This was an artifact due to the presence of carbon impurities whose peak partially overlapped the silver emission peak, thus lowering its relative value and giving an excessive and nonsignificant chlorine peak value.

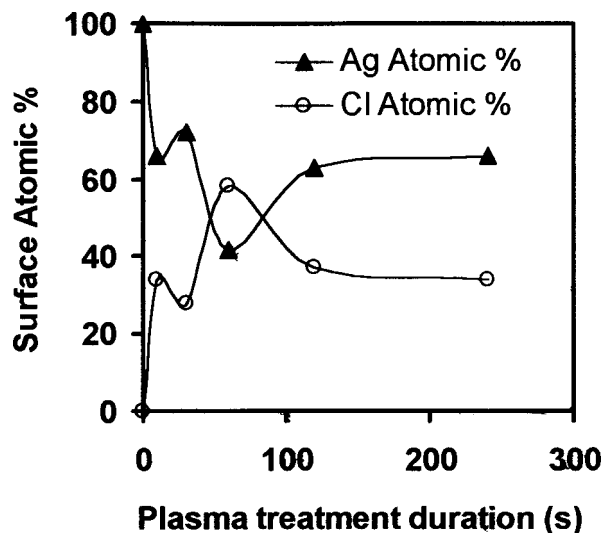


Figure 3. Atomic percentage of Ag and Cl detected at the surface of the sample, calculated from Ag MNN and Cl LVV energy peaks.

After plasma treatment chlorine was shown to remain at the surface and underneath it. Indeed, both Auger and XPS indicate a chloride bond formation rather than a weak absorption (creation of volatile species is limited since significant etching did not occur). According to literature,^{12,13} a 2.0-2.5 eV positive shift in the Auger silver peak can be attributed to a silver oxidized state due to the halogen bonding. The 2.3 eV shift observed here is further evidence that plasma treatment resulted in partial conversion of the Ag to AgCl, although the Cl/Ag surface concentrations (Fig. 3) indicated a deviation from exact stoichiometry. Care is required in interpreting these results as electron beam modification of the surface has been observed and was reported.⁸ Nevertheless, Matsunaga *et al.*⁹ have shown that several types of nonstoichiometric structure Ag_xCl_y can exist, with the possibility of interstitial Ag and cation vacancies¹⁴ leading to structural flexibility and higher conductivity. The stoichiometry has been found to be chlorine depleted, yet increasing the flux and hence the amount of chlorine appears to result in greater penetration rather than improved stoichiometry (Fig. 2b and c). Input power, which governs the plasma species concentrations and their kinetic energies, had a very limited influence on the amount of chlorine added to the Ag thin film. The plasma species reacting with the surface are expected to be, from laser based diagnostics,⁷ atomic Cl and Cl₂⁺ with a small fraction of Cl⁺. The role of different Cl species is being investigated and will be the object of a more detailed publication. Since the penetration of chlorine species into the growing Ag_xCl_y film is almost independent of power, the present results seem to suggest that atomic chlorine diffusion is the more dominant modification route, compared to reactive or neutral ion bombardment.

Conclusions

We have shown that partial conversion of Ag thin films into Ag/AgCl thin films is achievable through a plasma modification process. Chlorine plasma treatments are, therefore, a suitable technique for thin Ag/AgCl microarray sensors. Further work is required as understanding the chemical and physical reactions occurring at the thin film surface would be a key to substrate stoichiometry,

together with a better process control. To this end, high-resolution plasma characterization using laser induced fluorescence, Langmuir probe techniques, optical emission spectroscopy, and photodetachment are currently underway and will enable the authors to correlate the surface properties to the flux and energy of impinging chlorine species.

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